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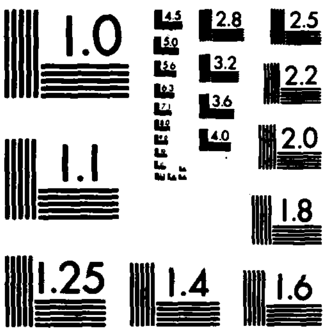

MICROCOPY RESOLUTION TEST CHART
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TECHNICAL
REPORT
NCSC TR383-83

DECEMBER 1983

TOTAL HALOGENATED HYDROCARBONS IN DIVERS BREATHING AIR

AD A136884

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ADMINISTRATIVE INFORMATION

The investigation described in this report was performed during fiscal year 1983 as an IR/IED task. The objective of this investigation was to develop methodology for total halogenated hydrocarbon analysis in Navy divers' breathing air.

Released by
M. F. Dannecker, Head
Product Engineering Test Division

Under authority of
C. M. Callahan, Head
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report covers an investigation of halogenated hydrocarbons in Navy divers' breathing air. It covers compounds which have been found in divers' breathing air and their maximum observed concentrations. The OSHA limit of these compounds and the effects of the pressure on these limits is covered. Various detection techniques are discussed with a recommendation for a detector system which will detect these compounds as a group on a pass or fail basis. A recommended method for expressing total halogenated hydrocarbons as a group is also presented.

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INTRODUCTION

The breathing air of the US Navy diver is routinely analyzed to ensure that it meets the minimum requirements for purity established by the Bureau of Medicine and Surgery as set forth in the Navy Diving Manual.[1] However, the present standards for allowable contaminants are deficient because they do not cover the large and potentially dangerous group of contaminants that fall under the classification of halogenated hydrocarbons. These compounds have an accumulative effect on the body, normally in the form of damage to the kidneys, liver, and lungs. Individual compounds may also be a narcotic, carcinogenic, or irritant and may alter blood chemistry or have other specific health effects.[2]

There is an increasing possibility of encountering halogenated hydrocarbon compounds due to their expanding use. They are used as cleaning solvents, are contained in many types of rubber and plastic products, and can be produced by thermal decomposition of certain polymeric materials. Chlorinated hydrocarbons are often used to give flammability resistance to solvent formulations. They are inherently good solvents for polymers and other organic materials. Chlorofluorocarbons are in common use as refrigerants, fire extinguishing agents, aerosol propellants, degreasers, cleaners, and general solvents. This usage is also expanding to include selected bromofluorocarbons. In addition, a few iodohydrocarbons are used as sanitizing agents. The use of volatile halogenated hydrocarbons, particularly in the C_1 to C_3 range, has greatly increased. Since these compounds are used in many products and processes today, we can expect to find them in increasing amounts in divers' breathing air.

The Occupational Safety and Health Administration (OSHA), for protection of the industrial worker, has set limits for many of these halogenated hydrocarbons ranging from 0.1 ppm to 1000 ppm. The OSHA limit is for a maximum allowable exposure for an 8-hour day, 5-day work week. Divers are not exposed for 8 hours a day, 5 days a week; however, during their exposure they are subject to the deleterious effects of increased total pressure of depth. Therefore, adjustments to these limits may be required to allow for the increased solubility of these components in the body fluids due to their increased partial pressure.[3]

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[1] US Navy Diving Manual, Volume 1, NAVSHIPS 0994-001-9010, Third Edition, September 1973.

[2] Sax, N. I., Dangerous Properties of Industrial Materials, Fourth Edition, Van Nostrand Reinhold, New York, 1975.

[3] Purer, A., "Gas Analysis Requirements to Reach Depths in Excess of 1800 Feet," Divers Gas Purity Symposium Proceedings, Battelle, Columbus, Ohio, 1976.

The OSHA limits have constantly changed over the past few years; among the compounds of greatest concern are the halogens. Key federal regulatory boards are now organizing for a coordinated attack on hazardous chemicals and other substances. The Consumer Product Safety Commission, Environmental Protection Agency, Food and Drug Administration, and Occupational Safety and Health Administration recently formed the Interagency Regulatory Liaison Group (IRLG).

As a basis for action against target substances, IRLG has brought forth a 236-page document that includes a summary of regulatory actions already taken as well as plans for the future. There are many halogens on the IRLG list of dangerous substances including the following halogenated compounds:

Allyl chloride	Methyl chloroform
Carbon tetrachloride	Perchloroethylene
Chloroform	Polyvinyl chloride
Dibromochloropropane	Trichloroethylene
Epichlorohydrin	Vinyl chloride
Ethylene dibromide	Chlorofluorocarbons
Ethylene dichloride	

The decisions made by the IRLG could have a drastic effect on the diving community because several of the dangerous compounds are used as cleaning agents.

The paucity of specifications for total halogenated hydrocarbons in the Navy Diver's Breathing Air Standards was recognized at the 1976 Diver's Air Purity Symposium by a panel of Navy experts, including medical representatives from BUMED, NEDU, NCSC, and an industrial hygenist from the Naval Environmental Health Center. Because of the large number of halogenated hydrocarbons, identification of specific compounds and determination of their concentrations is a time consuming, expensive undertaking. They must be subjected to comprehensive examination using a gas chromatograph, a procedure that is awkward, costly, and unavailable at many locations. Therefore, the Navy air purity panel recommended combining all halogenated hydrocarbons into one group similar to the total hydrocarbon group now listed in the Navy Diver's Breathing Air Standards. For this new group they recommended a screening limit of 5 ppm Total Halogenated Hydrocarbons (THHC). This recommendation has not been adopted by the Navy Diver's Breathing Air Standards because there is no established economical procedure for prescreening these compounds as a group. Also, a method of expressing THHC concentration has never been defined. The definition of THHC will require the acceptance of a specific halogenated hydrocarbon or some form of halogen equivalents as a standard of comparison and the determination of the relative sensitivity of the various halogens with this standard. This must be done on a detector system specifically for the halogens that may be encountered in divers' air.

ANALYSIS METHODS FOR HALOGENATED HYDROCARBONS

FID AND ECD METHODS

There are several methods of analyzing for halogenated hydrocarbons; each has advantages and disadvantages. The gas chromatograph column is useful with its unmatched capability for separating individual compounds. There are several detector systems such as the Flame Ionization Detector (FID) and the Electron Capture Detector (ECD) which can be located at the column exit; each is highly sensitive to the components of interest. The FID is not discriminatory; it responds to almost all organic compounds, although with somewhat lesser sensitivity to those with increasing proportions of halogens. The FID system has become the acceptable method for total hydrocarbon analysis. Its sensitivity is approximately equal to the number of carbons in the molecule. The ECD is more discriminatory, being highly sensitive to electronegative compounds such as halogenated hydrocarbons. However, it suffers from a very large variation of sensitivities for halogenated compounds. For example, carbon tetrachloride produces a response 7000 times that produced by an equivalent concentration of chlorobenzene. Such variation in sensitivity would not allow group analysis. The ECD also has the disadvantage of being sensitive to non-halogen compounds such as some unsaturated dibasic esters, aromatic aldehydes, nitroaromatic compounds, and unsaturated aromatic hydrocarbons. Another disadvantage is the requirement of an AEC license or permit.

OTHER METHODS

Other detection techniques that might be considered are mass spectroscopy, infrared spectroscopy and electronic spark (UV photography) which have disadvantages of high cost, inability to do group analysis, instrument complexity, and sensitivity.

TWO POSSIBLE DETECTION SYSTEMS

There are two detector systems which might be applicable to group type halogenated hydrocarbon analysis: the Dohrmann detector and the Freon leak detector.

Dohrmann Detector

The Dohrmann detector is a microcoulometric detector with a silver cell operating in the oxidative mode. It is specific for all halogens and halogen compounds except fluorine and its derivatives. The principle of operation is based on total sample pyrolysis in an oxygen stream at 950°C followed by coulometric titration. This detection system has been developed for high sensitivity and is capable of detecting halogens down to a low ppm range with a response that is related to the molecules halogen content. This would be a good candidate for a total halogenated hydrocarbon detector.

Freon Leak Detector

The Freon leak detector represents the detector system with the highest potential sensitivity for halogenated hydrocarbons. Its operation is based on the ionization of the alkali atom and is specific for all halogens; however, it exhibits reduced sensitivity for fluorohydrocarbons. This does not present a problem because all fluorohydrocarbons now used also contain chlorine or bromine which gives good response. The sensor consists of a ceramic material which has been pretreated with the carbonates of aluminum and rubidium before being heated to high temperatures. This ceramic material is placed on a cylindrical platinum container which is called the emitter. The collector is a platinum wire coil helically wound around the emitter and electrically insulated from it. This collector is heated to 900°C which in turn heats the emitter to a similar temperature. The presence of a halogen-bearing gas causes the rubidium to leave the emitter and become ionized on the heated platinum surface. A dc voltage impressed between the collector and emitter results in a current flow when the ionized rubidium is present. With no halogen molecules in the gas stream passing through the element, the current flow is very low. As the halogen gas concentration increases, the corresponding current increase is amplified to provide an output signal. This signal is related to both the concentration of the halogen gas and the number of halogen atoms in the individual molecules. Because of the low cost of this detector system, lack of any support material, and high specific sensitivity for halogen compounds, it is the most economical approach for group halogenated hydrocarbon analysis.

According to the manufacturer during the early development of this detector system they had considered developing a total halogenated hydrocarbon detector for OSHA. However, OSHA's wide selection of possible halogenated hydrocarbons encountered on an industrial-wide basis made it desirable to set limits on each individual component; hence, there was no requirement for a total halogenated hydrocarbon detector. In early investigations, the manufacturer had collected a large amount of data related to the sensitivity of this detector to various halogenated hydrocarbons (Table 1). Different detector designs are expected to produce somewhat different response. The data of Table 1, however, should be a good representation of what can be expected from a detector of this type.

HALOGENATED HYDROCARBONS OBSERVED IN DIVERS' AIR

The large number of halogenated hydrocarbon compounds made it desirable to limit the evaluation of instrument response to specific halogenated hydrocarbons that have been encountered in divers' air or related compressor-storage systems. This limitation of components reduced the gas standards required to a number of compounds that could be obtained and evaluated with the limited funds and time available. A review of the records of NCSC's SCUBA air and the OSF chamber gas analysis over the 1973 to 1983 time period plus

RELATIVE RESPONSE OF GENERAL ELECTRIC HALOGEN GAS MONITOR

Halogenated Compound	Sensitivity Relative To R-12	Halogenated Compound	Sensitivity Relative To R-12
Acetylene tetrabromide	4.00	Epichlorhydrin	1.50
Allyl chloride	1.50	Ethyl bromide	1.00
Benzyl chlorie	1.10	Ethyl chloride	1.00
Boron tribromide	3.00	Ethylene chlorohydrin	1.50
Boron trifluoride	0.02	Fluorine	0.02
Bromine	2.00	Fluorotrichloromethane (R-11)	3.40
Bromine pentafluoride	1.00	Hexachlorocyclopentadiene	7.00
Bromoform-Skin	3.50	Hexchloroethane	7.00
Carbon tetrachloride	4.60	Hexafluoroacetone	0.01
Chlorine	2.20	Hydrogen bromide	0.70
Chlorine dioxide	1.50	Hydrogen chloride	1.30
Chlorine trifluoride	1.00	Hydrogen fluoride	0.02
Chloroacetaldehyde	1.00	Lindane	7.00
α-Chloroacetophenone(phenacylchloride)	1.00	Methyl bromide	0.60
Chlorobenzene (monochlorobenzne)	0.90	Methyl chloride	0.60
o-Chlorobenzylidene	1.00	Methyl chloroform	4.00
malononitrile (OCBM)		4, 4'-Methylene bis (2-chloraniline)	2.00
Chlorobromomethane	1.60	Nitrogen trifluoride	0.01
Chloroform (Trichloromethane)	3.80	Oxygen difluoride	0.01
bis-Chloromethyl ether	2.00	Perchloromethyl mercaptan	4.00
1-Chloro-1-nitropropane	1.50	Perchloryl fluoride	1.00
Chloropicrin	1.00	Phosgene (carbonyl chloride)	2.00
Chloroprene (2-chloro-1, 3-butadiene)	2.00	Phosphorus trichloride	3.50
O-Chlorotoluene	1.00	Propylene dichloride (1, 2-Dichloropropane)	2.00
1, 2-Dibromoethane (ethylene dibromide)	2.00	Sulfur hexafluoride	0.01
Dichloracetylene	2.00	Sulfur monochloride	2.00
o-Dichlorobenzene	2.00	Sulfur pentafluoride	0.01
p-Dichlorobenzene	2.00	Sulfur tetrafluoride	0.01
Dichlorodifluoromethane (R-12)	1.00	Sulfuryl fluoride	0.01
1, 1-Dichloroethane	2.00	Tellurium hexafluoride	0.02
1, 2-Dichloroethane	2.00	Tetrachloroethylene	3.60
1, 2-Dichloroethylene	2.00	1, 1, 1, 2-Tetrachloro-2, (R112) 2-difluoroethane	4.00
Dichloroethyl ether	2.00	Trichloroethylene	3.00
Dichloromonofluoro methane (R-21)	2.50	Vinyl bromide	1.50
1, 1-Dichloro-1-nitroethane	2.00	Vinyl chloride	1.50
Dichlorotetrafluoroethane (R-114)	1.00	Trifluoromonobromomethane (Halon 1301)	0.50
Difluoromonochloromethane (R-22)	1.00	Difluorochlorobromomethane (Halon 1211)	1.00
Difluorodibromomethane	1.0		

those reported by C. L. Deuel and R. M. Roberts[4] on Naval hyperbaric diving gases revealed 17 contaminates (Table 2) associated with divers' air. Some of these components are the result of circulating breathing air in diving equipment for test purposes. Table 2 also lists the maximum observed concentration of these components in divers' air. This does not imply that divers have used air with these high contaminant levels. It means that the compressors had been overhauled or replaced, the storage flask and connecting piping had been cleaned, or other alterations had been made which made it mandatory to have the breathing air analyzed before being used by Navy divers. These maximum observed concentrations often exceeded the OSHA exposure limit (Table ' second column). Higher OSHA limits are often allowed for short time exposui for the industrial worker. Some short time exposure limits would probably applicable to the time duration of normal air diving. These limits are oft related to the individual component, thus the incorporation of them i allowable limits is beyond the scope of this report.

The last column in Table 2 lists the OSHA limits adjusted for the increased partial pressure due to the total pressure at a seawater depth of 200 feet. It is assumed that the 200-foot depth represents the maximum depth that air would be used for diving. These values are only a rough guide for maximum allowable exposure limits. They would have a safety factor since the OSHA limits that they were calculated from are based on an 8-hour exposure.

APPARATUS

The Ferret Freon leak detector manufactured by General Electric* meets the criteria of high specific sensitivity for halogenated hydrocarbons at low cost which encouraged its selection as the detector of choice. The flow system for this instrument is illustrated in Figure 1. The air sample is drawn into the probe assembly by a pump, operated by a synchronous motor, where it is mixed with halogenated hydrocarbon free air. This mixture is drawn into the manifold where it is divided into two gas streams. One stream is diluted with halogenated hydrocarbon free air from the filter before passing into the detector. This gas stream is returned to the manifold remixed with the second stream from the probe before being drawn into the pump for venting or recycling through the air filter. The sample dilution is designed to protect the sensor from exposure to 100 percent Freon and for temperature stabilization. It should be possible to reduce the sample dilution with a corresponding gain in sensitivity.

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[4]Deuel, C. L. and Roberts, R. M., "Complete Analysis of Naval Hyperbaric Diving Gases," Divers Gas Purity Symposium Proceedings, Battelle, Columbus, Ohio, 1973.

*Reference to names of specific equipment used are made to facilitate understanding and do not imply endorsement by the US Navy.

TABLE 2

HALOGENATED HYDROCARBONS ASSOCIATED WITH DIVERS' AIR

Halogenated Compounds	Max Observed Concentration in Divers' Air and Hyperberic Diving Gases (PPM)	OSHA Exposure Limit (PPM)	OSHA Exposure Limit at 200 ft Seawater (PPM)
Freon 11	25,980	1000	167.0
Freon 12	3,034	1000	167.0
Freon 113	38,489	1000	167.0
Methyl Chloride	48	100	16.7
Methylene Chloride	2,880	200	33.0
Chloroform	819	50	8.3
Carbon Tetrachloride	0.2	10	1.7
Ethyl Chloride	38	1000	167.0
Ethylene Dichloride	988	50	8.3
Trichloroethylene	521	100	16.7
Vinyl Chloride	3.5	1	0.2
Vinylidene Chloride	2,536	10	1.7
Perchloroethylene	2,801	100	16.7
Chlorobenzene	0.1	75	12.5
Freon 1112	11	*	*
Dichlorodifluoroethane	3.6	*	*
Methyl Chloroform	8,284	350	50

*OSHA limits not established.

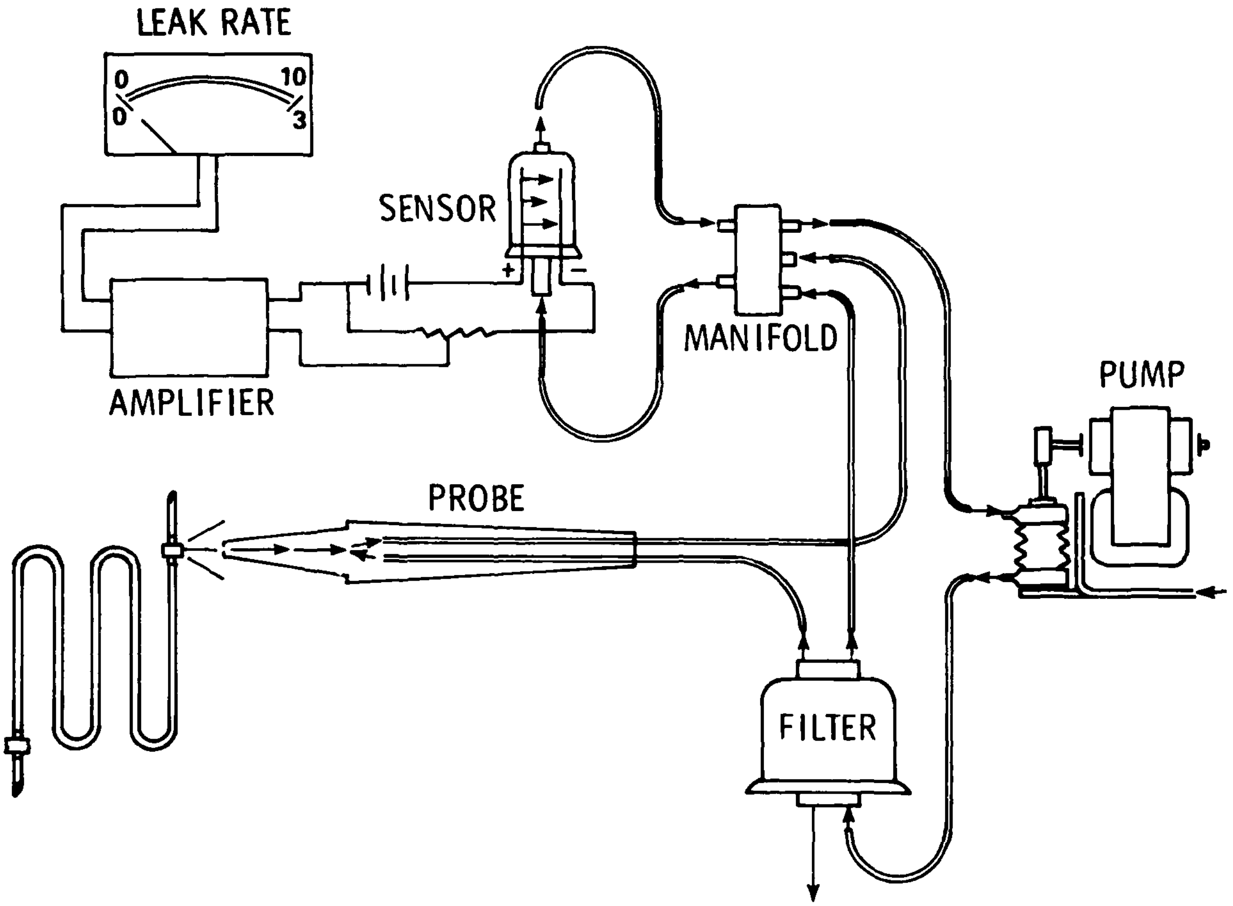

FIGURE 1. FLOW SYSTEM FOR THE FREON LEAK DETECTOP

An inlet system was constructed (Figure 2, to allow measurement of flow into the instrument and to assure that excess pressure was not used. This valve arrangement allowed a wide range of flexibility in sample introduction. Under normal operation, total flow was 85 to 100 cc/minute with 6 to 9 cc/minute going through the vent rotometer. The instrument's electronic circuit incorporated an automatic zeroing feature which cancelled out any signal output from the sensor at a rate of about 12 percent of full scale per second. This is a useful feature for the instrument when used as a Freon leak detector; however, this feature proved troublesome for our application. A halogen-free nitrogen gas supply was used to zero the instrument before each sample evaluation. A push-button switch mounted on the probe cancelled the automatic zeroing circuit at whatever zero it had adjusted to. Thus, caution was required to assure that a true zero had been achieved.

Gas standards for the 17 halogenated hydrocarbons observed in diver related air with concentrations ranging from 4 to 7 ppm were purchased from Scott Specialty Gases. All gas standards were prepared in nitrogen rather than air to reduce the possibility of interaction of reactive components with oxygen. To reduce or eliminate any interaction of sample components with the storage cylinders' inner walls, specially prepared aluminum cylinders were used.

DETECTOR SENSITIVITY FOR HALOGENATED HYDROCARBONS RELATED TO DIVERS' AIR

The alkali ion Freon leak detector was evaluated for its response to the 17 halogenated hydrocarbons related to divers' air. The sensitivities obtained are displayed in Table 3 as ppm (parts per million) per division of meter movement based on 10 divisions full scale. Very good sensitivity was observed for all components. Sensitivity tended to increase with an increase in the number of chlorine atoms in the molecule and decrease in the presence of fluorine. Also shown in Table 3 is the number of divisions that would be obtained theoretically if a sample containing the OSHA limit was injected into the detector system. In reality some of the high values would never be obtained since the high concentration of the halogen gas passing through the detector would result in the use of the ions being released from the emitter at a higher rate than they can be generated. Thus, a corresponding drop in sensitivity would be observed. This limitation would not affect the use of this instrument since the allowable limit for halogenated hydrocarbons will probably be in the range of 5 to 10 ppm. Such high concentrations would simply drive the reading off scale; thus, the sample would exceed the allowable limit and be rejected. Carbon tetrachloride, which is the most toxic component in divers' breathing air, would have a respectable 46-division output for its OSHA limit. Even adjusting for the increased effect of partial pressure at 200 feet of seawater would put the limit at about 7.6 divisions. Thus, this instrument meets the sensitivity requirement.

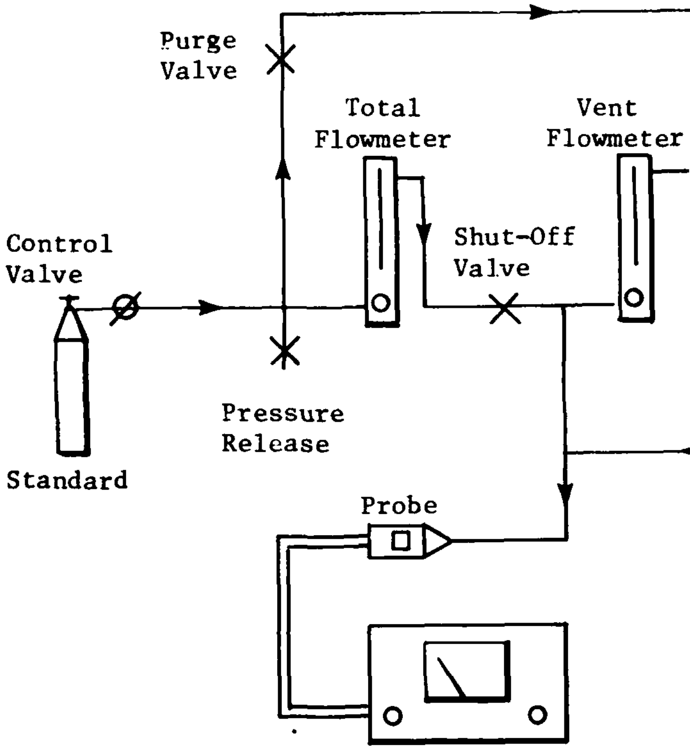

FIGURE 2. SAMPLE INLET SYSTEM FOR FREON LEAK DETECTOR

TABLE 3

FREON LEAK DETECTOR SENSITIVITY FOR HALOGENATED HYDROCARBONS OBSERVED IN DIVERS' AIR

Common Name	PPM/Div.	Division for OSHA Limit
Freon 11	0.26	3846
Freon 12	0.51	1961
Freon 113	0.17	5882
Methyl Chloride	0.98	102
Methylene Chloride	0.37	541
Chloroform	0.29	172
Carbon Tetrachloride	0.22	46
Ethyl Chloride	0.67	1493
1 2-Dichloroethane	0.45	111
Trichloroethylene	0.26	385
Vinyl Chloride	0.39	3
1 1-Dichloroethylene	0.28	36
Tetrachloroethylene	0.37	27
Chlorobenzene	2.2	34
Freon 1112	0.43	*
Dichlorodifluoroethane	0.43	*
Methyl Chloroform	0.29	1207

*OSHA limits not established.

Vinyl chloride has a lower OSHA limit (0.1 ppm) than carbon tetrachloride; however, this component was observed only in recirculated air. It was an offgasing product of polymeric material used in construction of the dive system. Normal SCUBA air is not recirculated; thus, vinyl chloride would not be considered an expected contaminate.

Sensitivities versus number of chlorines in the molecule for halogens found in divers' air are plotted in Figure 3. This shows that sensitivity increases with the number of chlorines in the molecule. The spread-out effect is due to the fluorine content of the molecule. This curve shows that all halogen components encountered in divers' air give an acceptable sensitivity response. The lowest sensitivity was obtained from chlorobenzene with a 2.2 ppm/division; however, with an OSHA limit of 75 ppm it would be adequately represented.

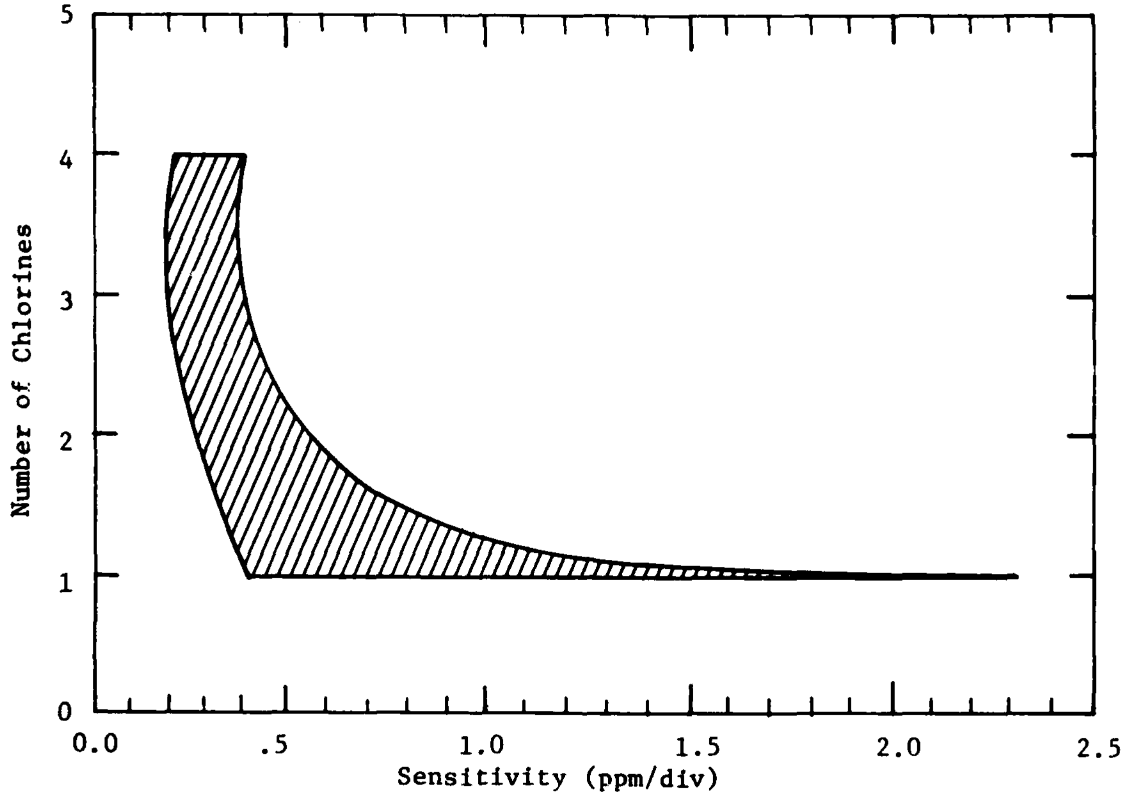

FIGURE 3. SENSITIVITY FOR HALOGENS FOUND IN DIVERS' AIR

From the manufacturer's data (Table 1), it was observed that the instrument has the same sensitivity for compounds containing bromine as it does for chlorine. Our investigation with a standard containing an iodohydrocarbon indicates that iodine would give the same response as chlorine and bromine.

METHOD OF EXPRESSING TOTAL HALOGENATED HYDROCARBON CONCENTRATION

The detector's output normally represents the combined response of several halogenated hydrocarbon species each with a different sensitivity factor. The problem then is to agree upon a standard method of expressing this output. Total hydrocarbons are expressed as methane equivalents. A

similar method needs to be derived for expressing total halogenated hydrocarbon concentration (THHC). Methane represents the simplest hydrocarbon. If similar logic is applied to THHC, the method of expression would be methyl chloride equivalents. With hydrocarbons, only one species of carbon exists; however, with halogen there are several species; viz., fluorine, chlorine, bromine and iodine; therefore, it would probably be more correct to express THHC as methyl halogen equivalents.

A method that has been used is to express THHC relative to Freon 12. This is due to the large amount of Freon 12 used for refrigeration and the fact that leak standards are based on the amount of Freon 12 that will leak out of a standard leak.

For THHC as applied to divers' breathing air, the term methyl halogen equivalents could be shortened to halogen equivalents with the understanding that the instrument would be standardized with methyl chloride or its equivalent. Table 4 shows the THHC expressed as methyl halogen equivalents that would be obtained at the OSHA limit for the detector used in this report. Sensitivity of other similar instruments may vary slightly due to different gas dilution or detector operating temperatures.

The general trend is for detection output to increase with increasing number of chlorine, bromine, or iodine atoms in the molecule. The lack of sensitivity for fluorine does not present a problem for this application since all components encountered in divers' air that contain fluorine also contain other halogens for which the detector has high sensitivity. Since the halogens chlorine, bromine, and iodine free rubidium ions on a one-for-one basis, the instrument has about equal sensitivity for these components. Thus, the instrument is a halogen counter at low concentrations for non-fluorinated hydrocarbons with a linear output that is specific for each individual organic family.

Figure 4 and Table 5 show this relationship for both the General Electric data and the experimental results. The linear relationship was good for all components evaluated at the 4- to 7-ppm range except the experimental results of ethylene with four chlorines. Tetrachloroethylene's initial response was acceptable; however, it slowed down with time and never leveled off even after a continuous inlet flow of several minutes. This data point is shown in Figure 4, but it was not used in the experimental straight line plot.

Sensitivity changes with varying fluorine content on the methane molecule containing one through four chlorines or bromines are displayed in Figure 5. This effect is unpredictable ranging from none to both small increases and decreases in sensitivity.

Figure 6 shows that increasing the number of carbons in the molecule while holding the chlorine or bromine constant has little effect on sensitivity for a given organic family. The sensitivity can be affected by the presence of NO, O, and OH groups in the molecule. These effects can range from none to slightly increased response.

TABLE 4

EXPERIMENTAL DATA FOR METHYL CHLORIDE EQUIVALENTS

Halogenated Compounds	Relative Sensitivity to Methyl Chloride	OSHA Exposure Limit (PPM)	Division for OSHA Limit (Div)	Methyl Chloride (PPM) Equivalents
Freon 11	3.8	1000	3846	3800
Freon 12	1.9	1000	1961	1900
Freon 113	5.8	1000	5882	5800
Methyl Chloride	1.0	100	102	100
Methylene Chloride	2.6	200	541	520
Chloroform	3.4	50	172	170
Carbon Tetrachloride	4.5	10	46	45
Ethyl Chloride	1.5	1000	1493	1500
1 2-Dichloroethane	2.2	50	111	110
Trichloroethylene	3.8	100	385	380
Vinyl Chloride	2.5	1	3	3
1 1-Dichloroethylene	3.5	10	36	36
Tetrachloroethylene	2.6	100	250	25
Chlorobenzene	0.4	75	34	30
Freon 1112	2.3	*	*	
Dichlorodifluoroethane	2.3	*	*	
Methyl Chloroform	3.4	350	1207	1190

*OSHA limits not established.

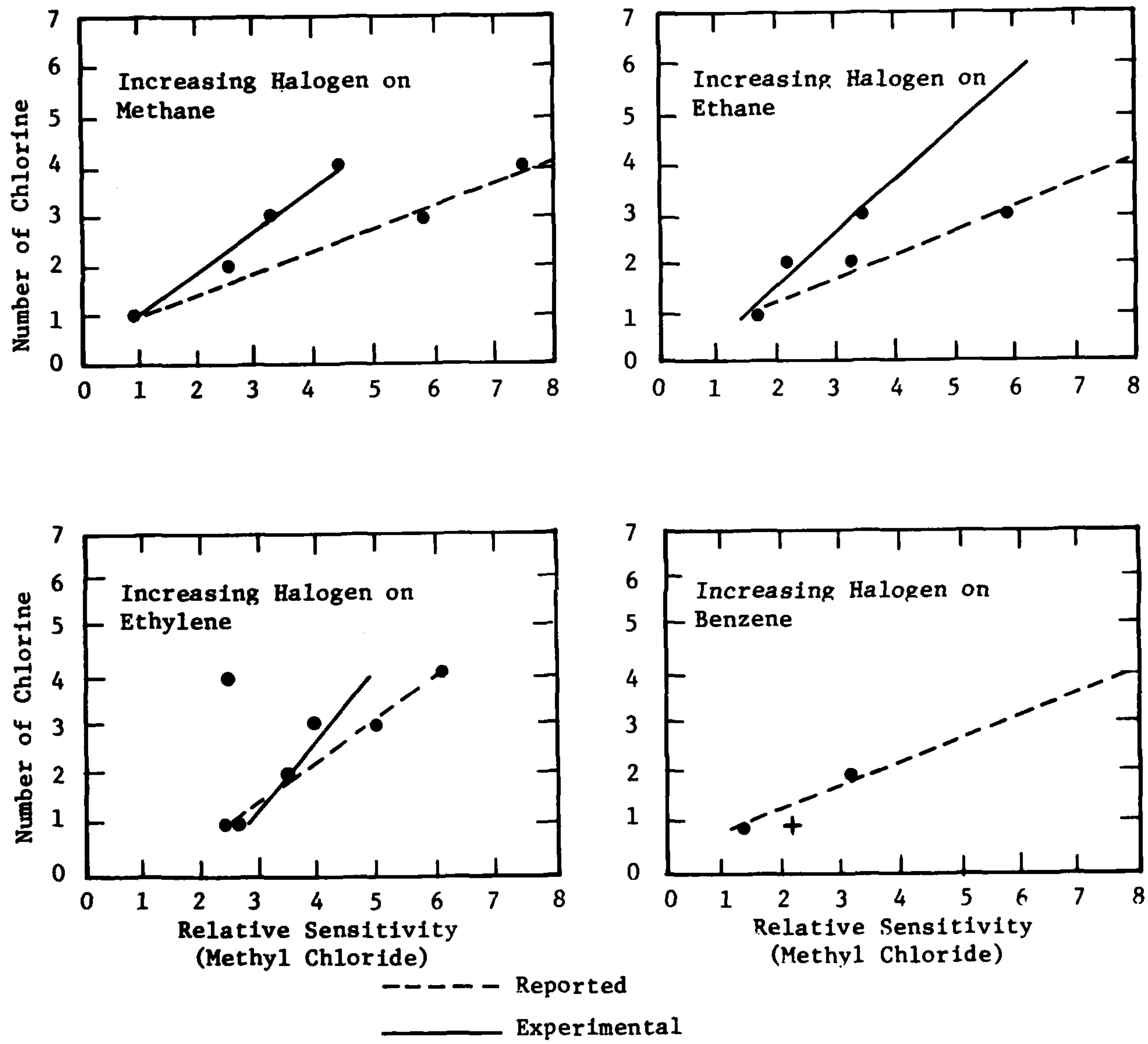

FIGURE 4. DETECTOR RESPONSE TO NONFLUORINATED HALOGENATED HYDROCARBON FAMILIES

TABLE 5

DATA USED FOR GRAPHS IN FIGURE 4

Compound	Number of Chlorines	Experimental Sensitivity	Reported Sensitivity
Methyl Chloride	1	1.0	1.0
Methylene Chloride	2	2.6	
Chloroform	3	3.4	5.9
Carbon Tetrachloride	4	4.5	7.5
Vinyl Chloride	1	2.5	2.5
1 1-Dichloroethylene	2	3.5	
Trichloroethylene	3	3.8	4.9
Tetrachloroethylene	4	2.6	5.9
Ethyl Chloride	1	1.5	1.7
1 2-Dichloroethane	2	2.2	3.3
Methyl Chloroform	3	3.4	5.9
Chlorobenzene	1	0.4	1.5
Dichlorobenzene	2	-	2.0

NOTE: Sensitivities listed in this table are relative to Methyl Chloride.

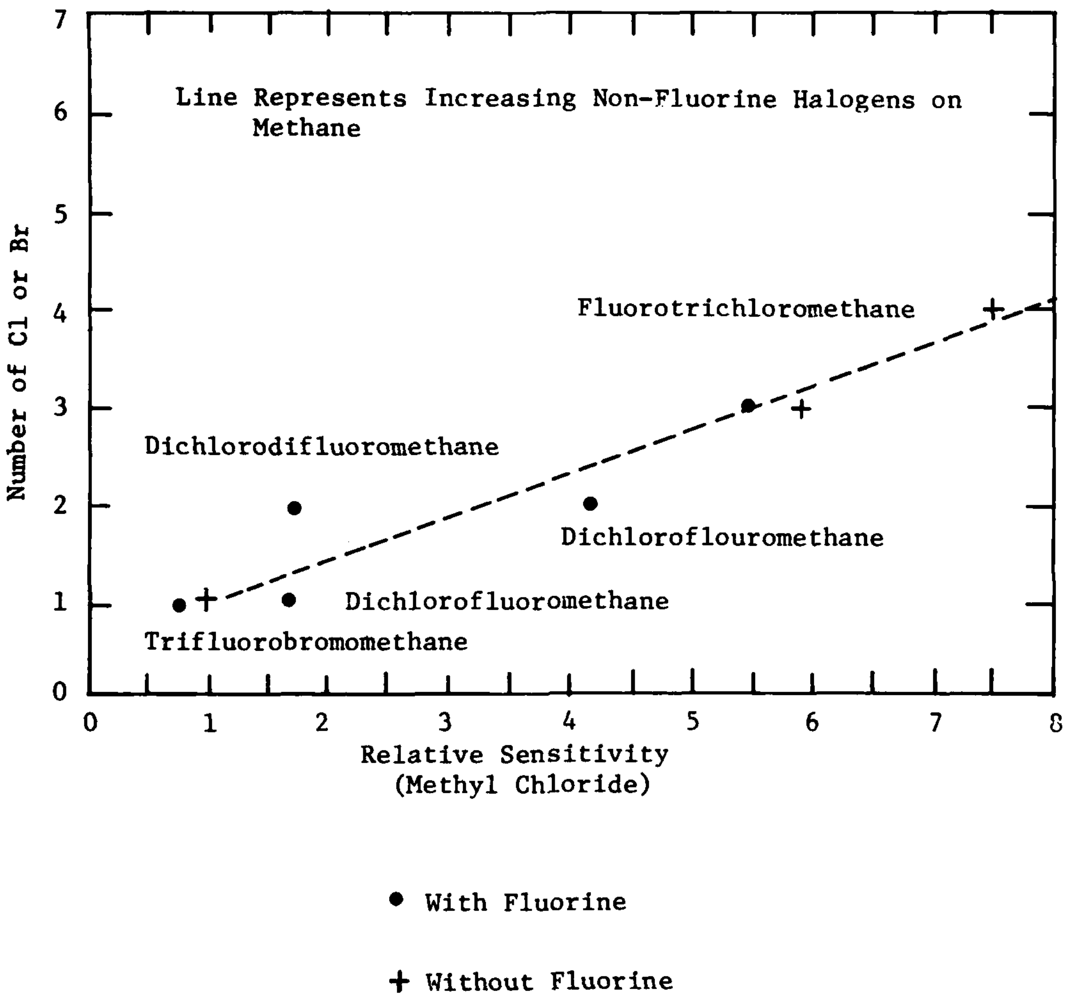

FIGURE 5. SENSITIVITY CHANGES WITH VARYING FLUORINE CONTENT

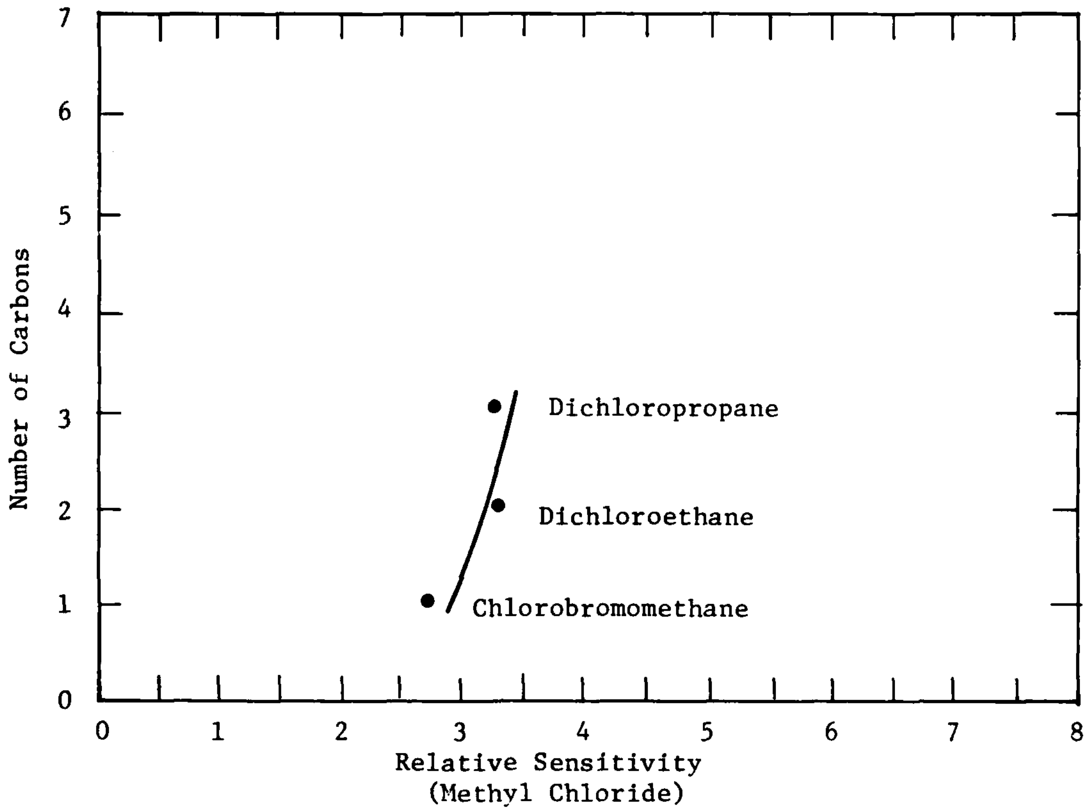

FIGURE 6. EFFECTS OF INCREASING CARBON WITH A CONSTANT NUMBER OF HALOGENS

CONCLUSIONS

This investigation revealed that halogenated hydrocarbons occasionally are found in Navy divers' breathing air. It identified 17 of these components, some of which have long term adverse health effects such as damage to the kidneys, liver, and lungs. A detector system specifically for these halogens with adequate sensitivity for detecting these components on a pass or fail basis was described along with recommendations for instrument optimization. A recommended procedure for expressing THHC concentration was also developed.

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